Attorney Docket No. P66718US0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: ANTON et al.

Application No.: 09/857,181 Group Art Unit: 1772

Filed: June 19, 2001 Examiner: Patricia L. Nordmeyer

For: MICROPOROUS HEAT INSULATION BODY

SECOND DECLARATION UNDER 37 CFR. 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

The undersigned Octavian ANTON does hereby declare and state that:

1. He is named inventor of the subject application.
2. He attended University of Bucharest, Romania, Faculty of Geology and Mineralogy, first graduating therefrom in 1962, receiving therefrom the degree Ph.D. in Mineralogy in 1970, and a post-doctorate graduate work in physico-chemical analytical techniques in 1971.
3. He worked from 1962 to 1964 with a geological prospection enterprise, from 1964 to 1972 as a researcher at the Geological Institute of the Romanian Academy of Science, and from 1972 to 1975 as a researcher at the Geological Institute of Romania involving clay mineralogy; in 1975 he became an Assistant at the Catholic University Louvain-la-Neuve, Belgium; and from 1976 to the present he has worked at Etex Group (formerly S.A. Eternit N.V.) – initially working in the field of mineral synthesis for applications in the building industry at the research center of S.A. Eternit N.V., in 1990 becoming Research and Development (R&D) Deputy Director, and currently holding the position Director, Promat

International Research and Technology Centre, Promat International NV (an Etex Group company), responsible for executing, supervising, and coordinating R&D activities in Belgium, England, and Austria for new products, and a new generation of products, in the fields of fire protection and high temperature insulation.

4. He is founder and past-president of the Romanian Clay Minerals Group and a member of the i.c., International Association for Clay Studies.

5. He is named inventor of a number of patents in the fields of fire protection, synthetic mineral structures for application in chemical and bio-chemical catalysis, friction materials, and plastics.

6. In connection with the subject patent application, he had personally supervised research with the objective of overcoming weaknesses in commercially available super-insulators based on pyrogenic silica.

7. He is familiar with the Office Action mailed December 2, 2002, including the rejection of claims under 35 USC 103(a), and the subsequent Advisory Action mailed September 3, 2003, maintaining the rejection under 35 USC 103(a), in the subject application and, in order to overcome the rejection, reports the following tests conducted and test results obtained under his direction and control:

The tested compositions:

- all percentages are by weight (w/w)

Invention Example 1 (dry mixture)

The dry mixture consists of 10% dry xonotlite (Promaxon®), 25% rutile (used as opacifier) – 3% silica-fibres- 62% pyrogenic silica.

The powders are mixed during 3 minutes in a Kenwood mixer and then pressed at a density of 0.300g/cm³. The pressure applied was 1MPa.

Comparative Example 1a (wet mixture)

For the preparation of the wet mixture, the pyrogenic silica, silica-fibres and rutile are mixed as described above for the dry mixture. This powder mixture is then added to a slurry of xonotlite in water. The xonotlite-slurry used was the slurry normally produced for Promat Ca-silicate-based fire protection boards, slurry similar to known xonotlite slurries used by industry to produce fire protection or high temperature insulation materials.

This wet mixture, which contains 50% dry phase and 50% water, is homogenized for 3 minutes and then pressed on a filter press applying a pressure of 1MPa.

Invention Example 2 (dry mixture)

5% Xonotlite powder, 3% silica-fibres, 25% ZrSiO4, and 67% pyrogenic silica are homogenously mixed by a planetary mixer (type Kenwood). The resulting dry mixture is then put into a mold, and pressed to form a monolithic sample. The formed sample is easily demolded. It has a good surface aspect, no surface cracks, dimensional stability, and no drying shrinkage afterwards. Dry density of the sample is 0,350g/cm³, and it has superior insulating properties. The sample material can be used as a product.

Comparative Example 2a (wet mixture)

As in Invention Example 2, 5% xonotlite powder, 3% silica-fibres, 25% ZrSiO4, and 67% pyrogenic silica are homogeneously mixed by a planetary mixer (type Kenwood), but the

xonotlite is in an aqueous (xonotlite) slurry (water content=89%). The amount of the mixture expressed by dry weight is kept the same as in Invention Example 1. The resulting wet mixture is then put into a mold and pressed to form a wet sample. After being dried at 60-105 °C, the sample shows slight drying shrinkage, with visible micro cracks on its surface. Dry density of the sample is 0,400g/cm³. The sample material cannot be used, directly, as a product.

Invention Example 3 (dry mixture)

40% Xonotlite powder, 3% silica-fibres, 25% ZrSiO4, and 32% pyrogenic silica are homogeneously mixed by a planetary mixer (type Kenwood). The resulting dry mixture is then put into a mold, and pressed to form a monolithic sample. The formed sample is easily demolded. It has a good surface aspect, no surface cracks, dimensional stability, and no drying shrinkage afterwards. Dry density of the sample is 0,350g/cm³, and it has superior insulating properties. The sample material can be used as a product (Appendix, Fig. 4 and Fig. 5).

Comparative Example 3a (wet mixture)

As in Invention Example 3, 40% xonotlite powder, 3% silica-fibres, 25% ZrSiO4, and 32% pyrogenic silica are homogeneously mixed by a planetary mixer (type Kenwood), but the xonotlite is in a (xonotlite) slurry (water content=89%). The amount of the dry mixture is kept the same as in Invention Example 2. The resulting wet mixture is then put into a mold and pressed to form a wet sample. After being dried at 60-105°C, the sample shows much drying shrinkage and it has an inferior surface aspect; no dimension tolerance can be controlled (Appendix Fig. 4 and Fig. 5). Dry density of the sample material is 0,500g/cm³; accordingly, it has a high thermal conductivity (=bad insulating properties). In addition, the material cannot be used, directly, as a product, and it needs to be sanded or cut to form a regular shape.

The parameters examined.

Integrity: the presence of cracks were checked by visual observation with a microscope and corresponding photographs taken, which are reproduced in the attached Fig. 1 and Fig. 2. The magnifications of the photographs in the attached Fig. 1 and Fig. 2 are indicated by scale bars below the photographs.

Thermal insulation: Lambda measurements were taken according to the hot-wire method with the KEM Model TC-51 High Temperature thermal conductivity meter (4 page meter brochure attached hereto). The measurements taken are recorded on the attached Fig. 3.

8. The tests and test results reported, herein, show that only the use of dry mixtures can lead to the production of a super-insulator. The wet method leads always to a standard type of insulator. The higher lambda values of the wet-processed system (Δ) relative to the dry system values (◇) recorded in Fig. 3 are due to the destruction of the nanoporous silica structure by capillary forces on drying.

9. The destruction of nanoporous structure following wet processing of pyrogenic silica is a known phenomenon and, for this reason, the art taught using sub-critical drying in conjunction with wet processing for such kinds of silica structures (for example, xerogels).

10. The use of xonotlite as a powder in a microporous heat insulation body as described and claimed in the subject application is the result of detailed research into insulation characteristics, targeting:

    (i) Improvement of de-airing during pressing a dry, micro-nanoporous mixture for manufacturing a super-insulation body. It is known that such mixtures shaped by pressing develop a spring-back phenomenon during de-molding, which destabilizes the shaped product's matrix. Addition of the xonotlite (Promaxon®) in the invention example is in accordance with the teachings of the subject invention application, as demonstrated by the test reported herein, and as described in the

subject patent application provides control of this phenomenon.

Previously the skilled person in the art solved this problem by sintering the product or by encapsulating the product in protective materials.

(ii) Improvement of bending strength: By eliminating the spring-back phenomenon, and due to the texture of xonotlite particles, bending strength is, also, improved for products such as super-insulators, which are known to be weak, difficult to handle, and to work with.

11. To achieve the aforesaid targeted insulation characteristics – i.e., those of a super-insulator – pyrogenic silica was found to be the best raw material. Pyrogenic silica is composed of nanoparticle aggregates having a nanoporous structure. The nanoporous structure is a key-parameter in the control of heat transfer through the finished super-insulator body.

12. When pressing a mixture containing pyrogenic silica, no contact with water is allowable, because the nanoporous structure is extremely sensitive and will be destroyed.

13. A salient feature of the xonotlite powder, in the invention described and claimed in the subject application, is the control of de-airing a pyrogenic-silica-based matrix during pressing in the manufacture of shaped, pyrogenic-silica-based products, e.g., an insulation body, for which, at equal density, the mechanical performance is also improved.

14. Accordingly, a very important feature of the invention described and claimed in the subject application is the pressing of mixtures in a dry condition. The matrix obtained by a wet process is totally different, both texturally and structurally, from the matrix obtained by a

dry process in accordance with the invention. These leads to totally different types of products with big differences in thermal insulation performance, as demonstrated by the experiments described above.

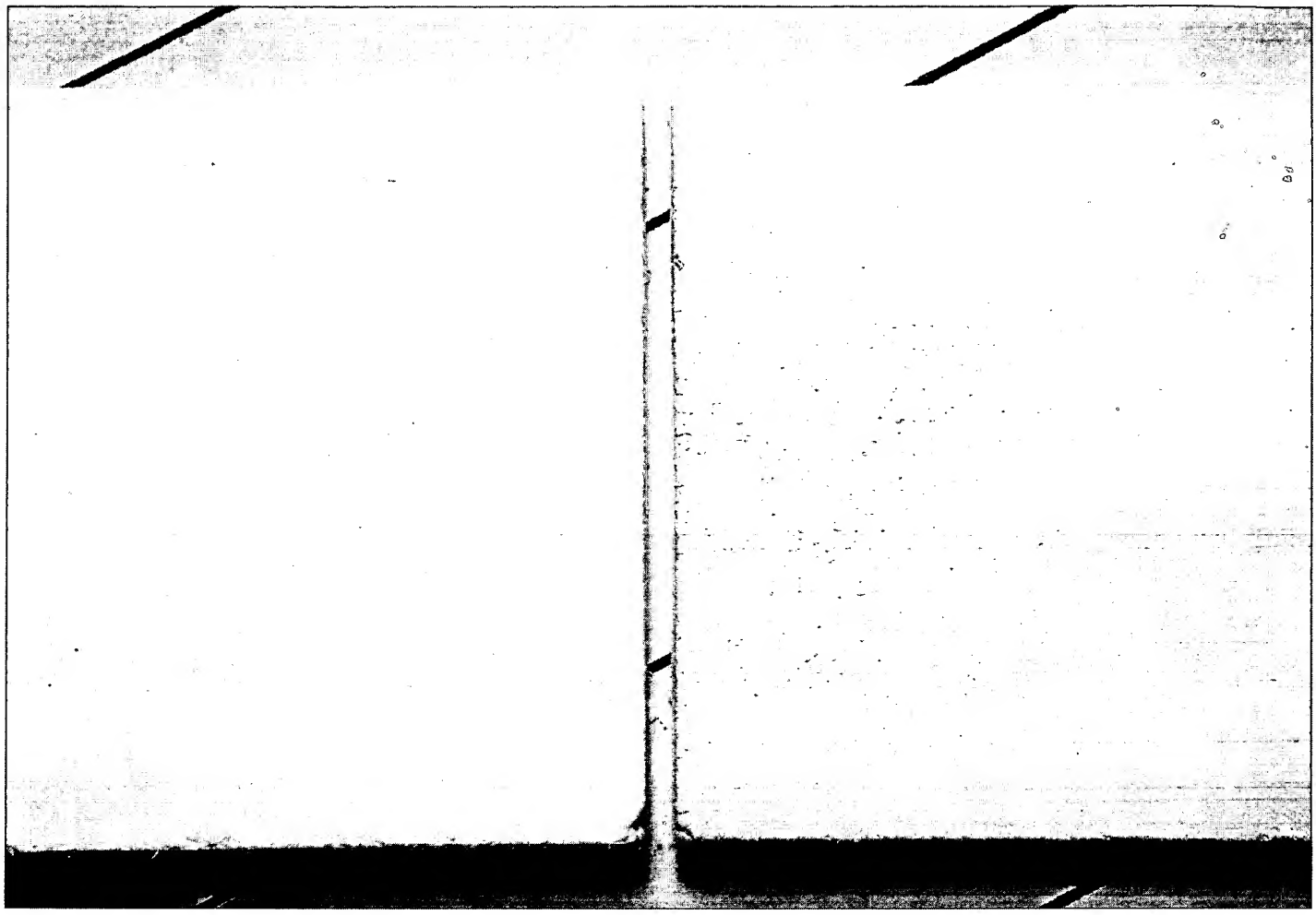
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements are made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the Unites States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

Further declarant sayeth naught.

19 NOV. 2004

Date

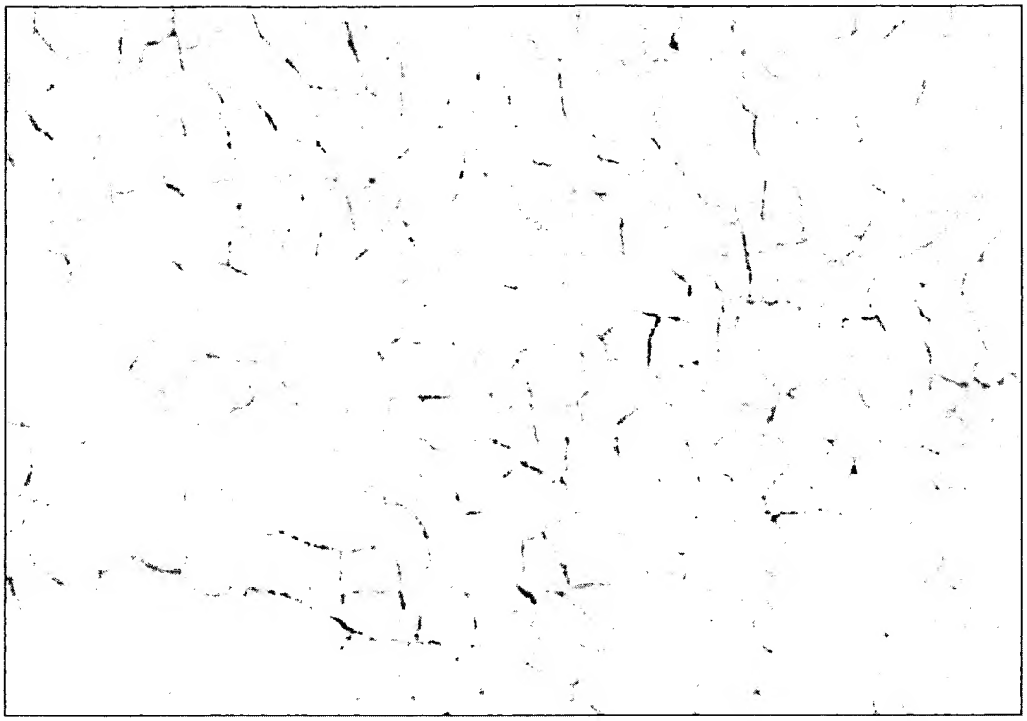
Octavian ANTON



1.6 cm

Left : sample with pyrogenic silica, fibres, opacifiers and xonotlite formed by dry pressing
Right : same mixture when wet processing is applied and in which cracking is observed. The structure at the right is more clearly visible in the detailed figure below.

Fig.1 : Differences in structure between samples formed by dry pressing (left side) and wet pressing (right side).



Detail at larger magnification showing the structure of a mixture with pyrogenic silica, fibres, opacifier and xonotlite, when the latter is added as a slurry.

Fig.2 : Differences in structure between samples formed by dry pressing (left side) and wet pressing (right side) seen at higher magnification.

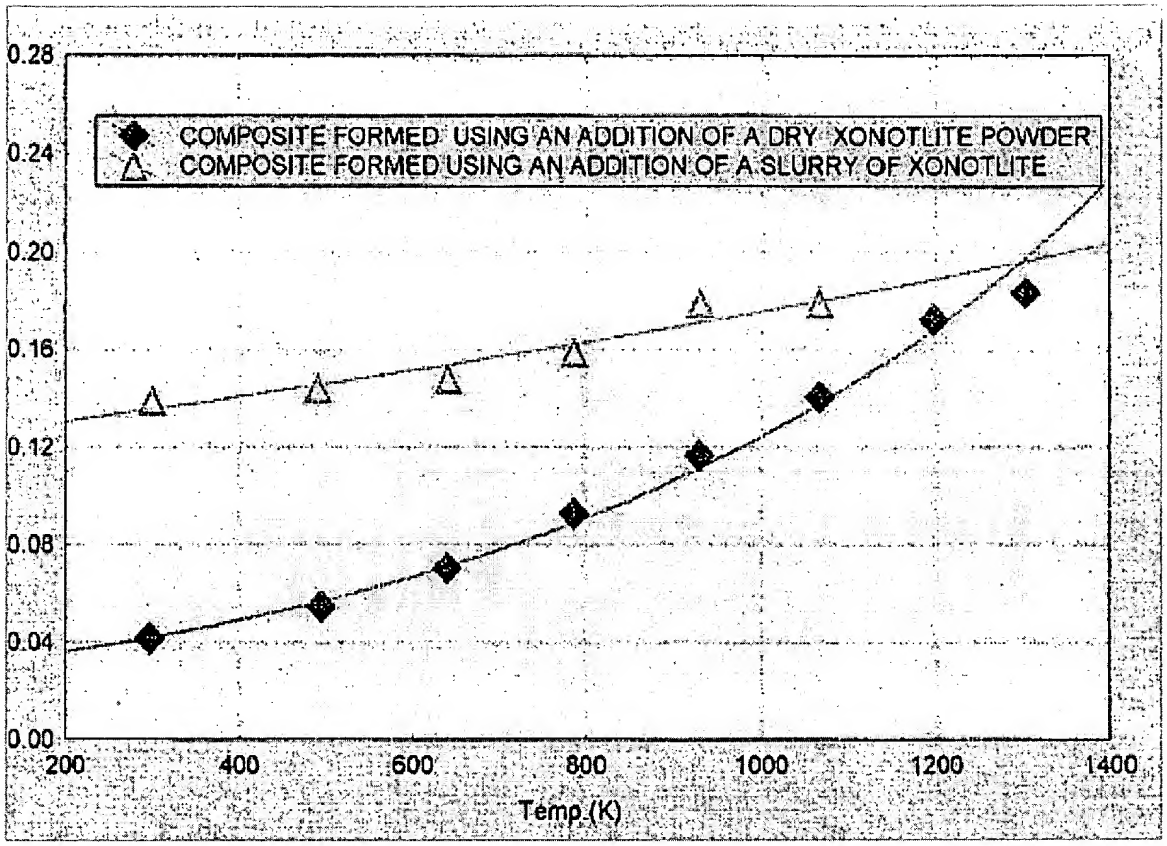


Fig. 3: lambda as a function of temperature for compositions made by dry pressing (♦) and wet processing (◊).

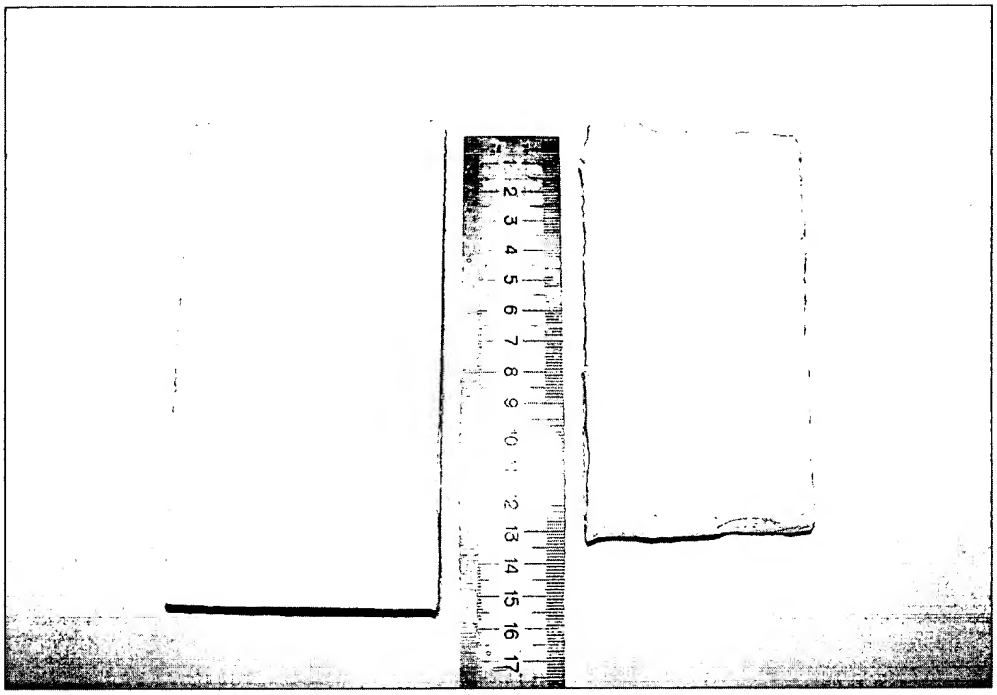


Fig. 4:
Sample on the left: prepared by dry pressing;
Sample on the right: prepared based upon wet Xonotlite

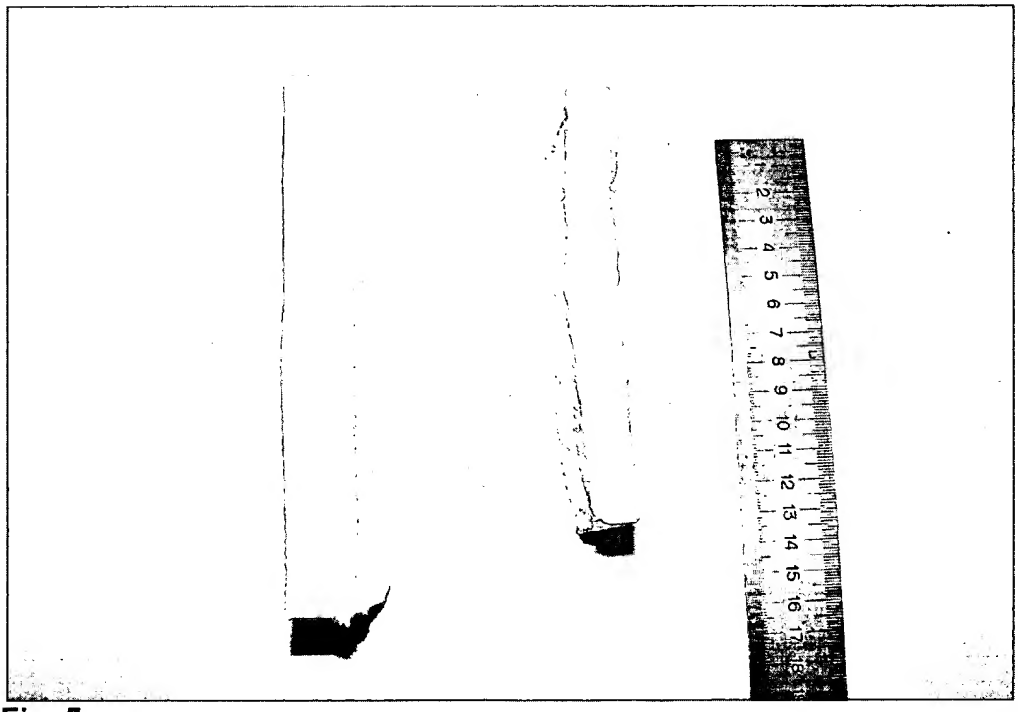


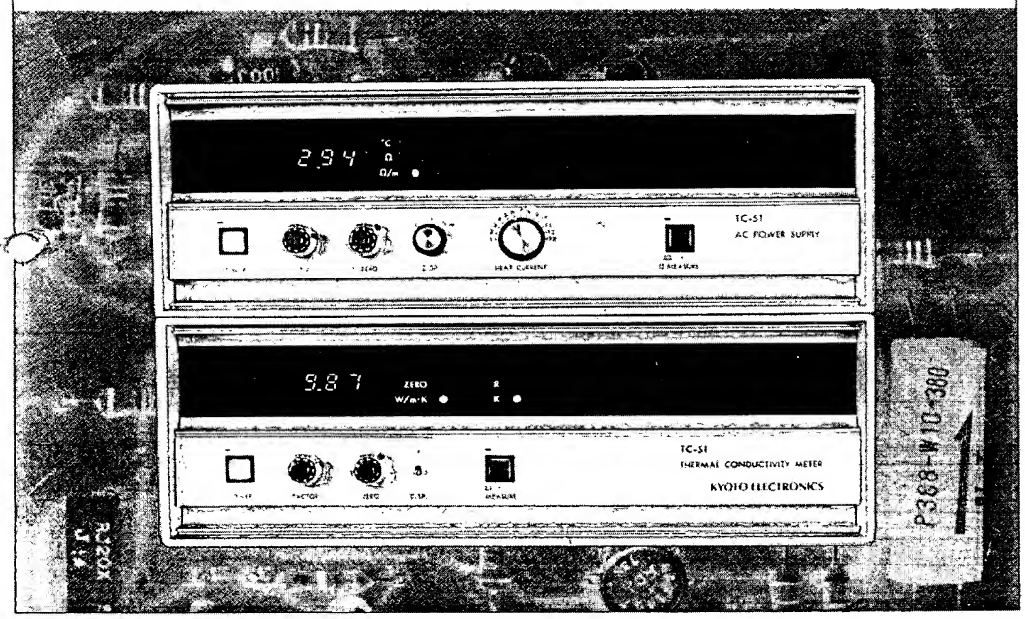
Fig. 5:
Sample on the left: prepared by dry pressing;
Sample on the right: prepared based upon wet Xonotlite

KEM

HIGH TEMPERATURE THERMAL CONDUCTIVITY METER

Lambda

model **TC-51**



KYOTO ELECTRONICS
MANUFACTURING CO., LTD.

Quick & Accurate Determination of Expanded Range of Thermal Condu

FEATURES

Measurement for High Temperature (Up to 1,500°C)

Employment of a high performance isolation amplifier permits measurement at an arbitrary temperature from 0°C to 1,500°C max by using the electric furnace. (Optional Accessory Model: EF-21)

Rapid and Accurate

Time actually required for measurement is approximately 200 seconds after the sample has reached the measuring temperature. This ensure measurements of good reproducibility with less effect of disturbance.

Easy Preparation of Samples

Two pieces of samples, Approx. 100 X 200 X 50 mm in size.

Direct Readout

No skill is required for operation and displays digitally the measured value of thermal conductivity.

Measurement for Electro-Conductive Materials

Samples indicating electro-conductivity at high temperature can also be measured by the employment of high performance AC constant-current heater circuit.

Automatic Calculation of the Heating Power

This apparatus functions to measure the resistivity of heating wire at measuring temperature, and calculate the heating power automatically.

OUTLINE

KEM Thermal Conductivity Meter is an apparatus to determine accurately in a short time with simple operation the thermal conductivity of solids such as refractories, glass, insulating materials, rubber, and plastics. The measured values are displayed digitally.

Thermal conductivity of solids is measured by the steady-state conduction method or unsteady-state conduction method. This apparatus is based on the latter method which employes a heating wire.

In the conventional steady-state conduction method, the sample is assumed to be ideal in composition and measurments should be carried out by keeping stable the temperature gradient from the heat source to the measuring point. Thus, measurements require skill and a long time, with difficulty and less reliability.

In the unsteady-state conduction method adopted for this apparatus, the thermal conductivity is measured by calculating the temperature increase of the heating wire before a thermal equilibrium is reached. A thin metal heating wire held between two samples gets hot due to Joule heat when an electric current is applied to it. (See Fig. 1)

The greater the thermal conductivity of a sample being measured, the faster the heat moves and dissipates and the less and slower the temperature rise of the heating wire. Conversely, samples of poor thermal conductivity dissipate heat less and permit the heating wire to get hot faster. (See Fig. 2) Thus, the thermal conductivity is determined based on the fact that the temperature rise of the heating wire varies depending on the thermal conductivity of the sample. This apparatus calculates the temperature rise of the heating wire and display digitally the measured value of thermal conductivity in terms of W/m.k.

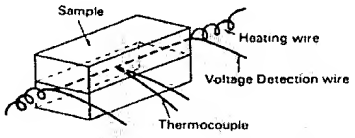


Fig. 1 Arrangement of sample, heating wire, voltage detection wire and thermocouple

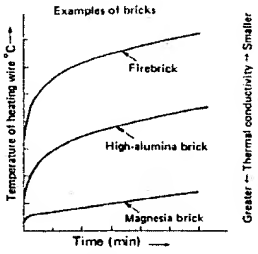
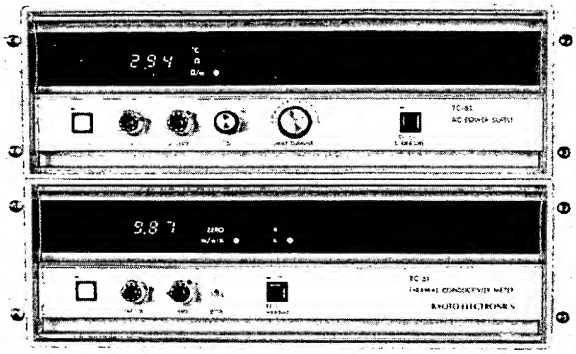
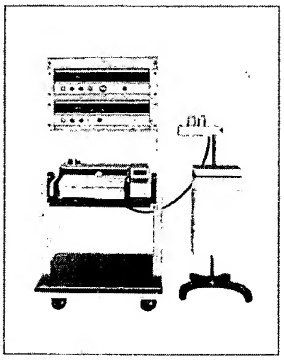


Fig. 2 Curves of temperature rise of heating wires

e High Temperature & vity





Specifications

Model	TC-51
Object for measurement	Refractory materials, Insulating materials, Ceramics etc.
Measuring system	Unsteady-state conduction method (Hot wire method)
Range of measurement	0.050 – 10.00 W/m.K
Display	Digital, 4-place
Reproducibility	within ±7%
Time required	Approx. 200 seconds (after the sample has reached the measuring temperature)
Output	DC 0 – 10 mV
Size of sample	Approx. 100 X 200 X 50mm, two pieces
Temperature range for samples	0 – 1,500°C (A well-insulated electric furnace is required for samples to be measured at temperatures higher than room temperature)
Detector	0 – 1,000°C / Heating wire ; Nichrome Thermocouple ; K (Chromel-Alumel) 400 – 1,500°C / Heating wire ; Platinum Rhodium Thermocouple ; R (pT–pT. Rhodium)
Power source	AC 100 ± 10V, 50/60Hz (other voltage available)
Power consumption	Approx. 100VA 100VA (Power consumption for an electric furnace is not included.)
Outside dimensions	Pre-Amprifier/Approx. 320(W) X 340(D) X 850(H)mm Caster /Approx. 530(W) X 600(D) X 1,207(H)mm
Composition	Main body with AC Power supply device/Pre-Amplyfire unit/Recorder/Caster/Sample stand with cover/Accessories case
Accessories	Heating wire with thermocouple for high temp. X 3/Heating wire with thermocouple for low temp. X 30/Platinum rhodium wire for compensation conductor X 2 meter/ Platinum rhodium wire for voltage detection X 2 meter/Electric welding device X 1/ Insulating tubes for detector X 1 set/Fuse X 2/Weight X 2/Instruction manual X 1.

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To : Analis S.A.

April 3, 1996

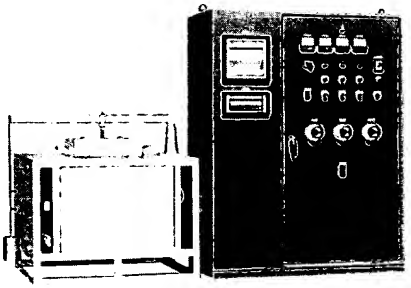
ADAPTOR FOR THERMAL CONDUCTIVITY METER

ELECTRIC FURNACE EF-21 (OPTION)

Specifications

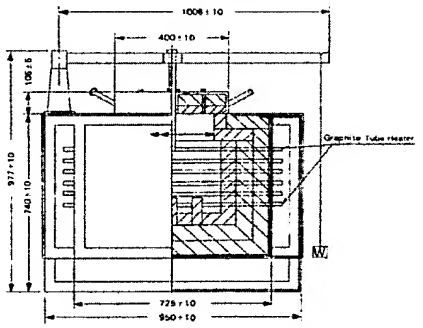
Electric furnace

Type	Crucible Type
Capacity	21 kW
Operating temperature range	400 – 1500°C
Maximum operating temperature	1600°C
Inside dimensions	Approx. 270(W) X 170(D) X 215(H) mm
Outside dimensions	Approx. 950(W) X 735(D) X 1000(H) mm
Heater	Graphite Tube



Temperature control distribution panel

Power requirement	AC 220V, 50/60Hz, 3-phase or AC 380V, 50/60Hz, 3-phase
Putput	7 KVA X 3 (single-phase)
Voltage contro	Automatic thyristor system (P.I.D. control)
Type	Self-supported
Others	With V meter, A meter, etc. 1 set
Outside dimensions	800(W) X 400(D) X 1580(H) mm
Color of finish	Munsell 7.5BG6/1.5



Temperature recording controller

Recording width	180 mm
Temperature scale	0 – 1800°C
Thermocouple	6 – 30Rh, 30cm With 5 m compensation conductor

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